

## DEACTIVATION OF DIRECT COAL LIQUEFACTION CATALYSTS BY CARBONACEOUS DEPOSITS\*

Frances V. Stohl and Howard P. Stephens  
Sandia National Laboratories  
Albuquerque, NM 87185

### INTRODUCTION

The accumulation of carbonaceous deposits on direct coal liquefaction catalysts has long been known to cause significant, rapid deactivation. We have previously shown that greater than 75% of the catalyst hydrogenation activity and 50% of the hydrodesulfurization activity is lost due to carbonaceous deposits within the first few days of coal processing.<sup>(1)</sup> The objective of the work reported here, which is part of a larger study aimed at extending catalyst life by mitigating the effects of carbonaceous deposits, was to determine the impact of several hydrotreater feed components and distillate cuts on catalyst activity. This work differs from previous studies<sup>(2,3)</sup> in that we have not only characterized the catalyst but have also quantitatively measured catalyst activity losses resulting from the contaminants. As a result of this study, we have found that losses of catalyst extrudate hydrogenation activity ranged from 23% for experiments with the lowest boiling fraction to 82% for a high boiling point feed component. Although HDS activity was not affected by the low boiling fraction, a 70% loss resulted from hydrotreating the highest boiling point component.

### EXPERIMENTAL PROCEDURES

Two process streams and various distillate cuts of a coal liquefaction hydrotreater feed were catalytically hydrogenated in microreactors. The starting feeds, products and catalysts of these experiments were characterized and the catalysts were tested for hydrodesulfurization and hydrogenation activities.

### Materials

The catalyst used in these studies was Shell 324M with 12.4 wt % Mo, 2.8 wt % Ni and 2.7 wt % P on an alumina support. The catalyst is in the form of extrudates measuring about 0.8 mm in diameter and 4 mm in length. Prior to use, the catalyst was presulfided with a 10 mol % H<sub>2</sub>S/H<sub>2</sub> mixture at 400°C and atmospheric pressure for 2 hours. The hydrotreater feed was obtained from the Wilsonville Advanced Coal Liquefaction R&D Facility's run 247 which processed Illinois No. 6 bituminous coal. This hydrotreater feed was made up of two process streams derived from the first stage thermal liquefaction unit. The two streams are identified by the number of the storage tank (V-178) and separator (T-102) from which they were obtained just before entering the hydrotreater. The V-178 process stream is lighter than the second process stream which consisted of the bottoms from T-102. Samples of each of these streams were used in this study. The feed to the hydrotreater at Wilsonville consisted of 35 wt % V-178 and 65 wt % T-102 bottoms.

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## Apparatus and Procedures

A Perkin-Elmer 36" adiabatic spinning band distillation column was used to separate V-178 into five boiling point fractions and to obtain boiling point information on the T-102 bottoms. Distillations were performed at 0.1 torr pressure. Boiling temperatures are reported as atmospheric pressure values.

Both process streams, the five distillate cuts, and a mixture of V-178 and T-102 bottoms comparable to the hydrotreater feed at Wilsonville, were each hydrotreated with presulfided catalyst in 40 cc microreactors at 350°C for 2 hours. The microreactors were charged with 6 g of feed, 2 g of catalyst and 1200 psig of H<sub>2</sub>. All of the feeds, products and catalysts from these experiments were analyzed for carbon, hydrogen, nitrogen and sulfur contents. The catalysts were Soxhlet extracted with tetrahydrofuran prior to analysis or activity testing.

Both hydrodesulfurization (HDS) and hydrogenation activities were determined for the catalysts. HDS testing was performed at atmospheric pressure and 350°C using a fixed bed flow reactor with thiophene as the model compound. HDS activity was measured by conversion to n-butenes and n-butane as analyzed by gas chromatography.

Hydrogenation activity was determined using the hydrogenation of pyrene to dihydropyrene as has been previously reported.<sup>(4)</sup> This testing was carried out in 26 cc microreactors at 300°C with 500 psig H<sub>2</sub> cold charge. Experiments performed on both catalyst ground to -200 mesh and whole extrudates enabled determination of the losses of both intrinsic and extrudate activities.

## RESULTS AND DISCUSSION

### Feed, Product and Catalyst Compositions

Results of distilling the two process streams showed that 96.1 wt % of the V-178 boiled below 850°F whereas only 16.4 wt % of the T-102 bottoms boiled below 825°F. The initial boiling points of the V-178 and T-102 bottoms were 400°F and 720°F respectively. The boiling point ranges and weight fractions of the five distillate cuts from the V-178 stream are given in Table 1, along with analyses on all the feed components. The most significant differences in elemental compositions between the V-178 and T-102 bottoms are the higher H/C ratio of the V-178 and the higher nitrogen content of the T-102 bottoms. The V-178 distillate fractions show decreasing H/C ratios with increasing boiling point.

Results of analyses of the products from the hydrotreating experiments are also given in Table 1. All of the microreactor products showed higher hydrogen contents and decreased nitrogen contents compared to the starting feeds. The greatest increase in H/C ratio was 28% for the run with T-102 bottoms. Products from all other experiments also showed increased H/C ratios between 9 and 14%. Hydrotreating a 35 wt % V-178 + 65 wt % T-102 bottoms mixture yielded an increase in hydrogen content that approximated that obtained by hydrotreating similar amounts of each stream separately. This indicates that the presence of the lower boiling process solvent did not improve T-102 bottoms hydrogen uptake.

Analyses of the catalysts retrieved from these runs are given in Table 2. These catalysts show an increasing carbon content with increasing boiling point of the feed processed. The nitrogen

content is highest on the catalyst used to process T-102 bottoms although all of the catalysts have at least 0.40 wt % nitrogen. All of the nitrogen removed from the V-178 feed was deposited on the catalyst whereas only 40% of the nitrogen removed from the T-102 bottoms was found on the catalyst. Processing of the V-178 + T-102 bottoms mixture yields a similar catalyst carbon content to processing the T-102 bottoms alone.

#### Hydrosulfurization Activity

HDS activity testing results obtained for whole catalyst extrudates from the microreactor runs are given in Figure 1. The standard deviation for this testing procedure is  $\pm 2\%$  absolute. Catalyst from the hydrotreating of the V-178 stream shows a small but statistically significant decrease in HDS activity compared to fresh catalyst. Catalyst used to hydrotreat T-102 bottoms, however, shows a 46% decrease in thiophene conversion which is equivalent to losing  $\sim 70\%$  of fresh catalyst HDS activity. Catalysts used in microreactor runs with the  $-550^\circ\text{F}$  and  $550\text{--}650^\circ\text{F}$  distillate cuts have the same HDS activity as fresh catalysts. HDS activities of catalysts from experiments with higher boiling point cuts decrease with increasing boiling point. Comparison of these results with the carbon deposition on the catalyst shows that catalyst carbon contents  $\leq 1.58$  wt % do not affect HDS activity. However, above this carbon content, HDS activity loss is proportional to carbon content. It is observed that the  $+850^\circ\text{F}$  portion of the V-178 causes significantly less carbon buildup and HDS activity loss than obtained with the T-102 bottoms which contain 83.6 wt %  $+825^\circ\text{F}$  material.

#### Hydrogenation Activity

A quantitative, mathematical expression, reported previously,<sup>(4)</sup> relates catalyst extrudate activity remaining (F) to the intrinsic activity loss ( $\alpha$ ). Use of the relationship between F and  $\alpha$  enables determination of the effective diffusivities of these catalysts. For catalyst from the run with V-178 feed, no significant decrease in effective diffusivity, as compared to fresh catalyst ( $5 \times 10^6 \text{ cm}^2/\text{sec}/\text{cm}^3$ ), was observed. However, catalysts from the run with the V-178 + T-102 bottoms mixture and from the run with only T-102 bottoms showed  $\sim 70\%$  decreases in effective diffusivity which are due to the higher carbon content of these catalysts. The relationship between F and  $\alpha$  enables differentiation of two limiting modes of deactivation--homogeneous and shell-progressive poisoning.<sup>(4)</sup> A plot of F vs  $\alpha$  for the effects of carbonaceous deposits alone is shown in Figure 2. Since the  $\alpha$  values increase more rapidly than the F values, the dominant mode of deactivation is due to homogeneous poisoning. A smaller F value indicates higher deactivation so that deactivation increases with higher boiling point of the microreactor feed. The catalysts used to hydrotreat T-102 bottoms and the V-178 + T-102 bottoms mixture have lost  $\sim 80\%$  of their hydrogenation activity after only 2 hours in the batch microreactor runs. The  $+850^\circ\text{F}$  component of the V-178 yields a 50% decrease in hydrogenation activity. The difference between the activities of the catalysts used to hydrotreat the  $+850^\circ\text{F}$  portion of the V-178 and the T-102 bottoms must be due to compositional differences between these high boiling point materials.

Comparison of the catalyst carbon contents in Table 2 with the  $F$  and  $\alpha$  values in Figure 2 shows that the greatest changes in  $F$  and  $\alpha$  as a function of carbon content occurred for the first sample with a carbon content of  $\sim 1.25$  wt %. Additional accumulation of carbon produces smaller changes of  $F$  and  $\alpha$ . There appears to be no correlation between losses of hydrogenation activity (or HDS activity) and nitrogen content of the catalyst.

#### CONCLUSIONS

Hydrotreating the high boiling materials for only 2 hours yielded up to  $\sim 80\%$  loss of hydrogenation activity and  $70\%$  loss of catalyst HDS activity. Combining a lighter solvent with the T-102 bottoms did not have any impact on the extent of deactivation. These results show that, in order to extend catalyst life, it is necessary to either eliminate the high boiling material from the hydrotreater feed or change the feed to eliminate the harmful components of these high boiling materials. Current studies are aimed at identifying and separating different chemical classes of compounds in the high boiling fractions to determine their individual effects on catalyst activity.

#### REFERENCES

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Table 1. Analyses of feeds and products from microreactor runs reported in weight percent.

Analyses of Hydrotreater Feed										
35% V-178 + 65% T-102		V-178 Distillate Cuts								
Distillate wt %		V-178	T-102 Bottoms	-550F	550-650F	650-750F	750-850F	850F+		
Carbon	87.16*	87.69	86.88	86.28	87.65	88.40	88.13	12.86	3.95	
Hydrogen	7.44*	10.05	6.03	10.62	10.14	9.75	9.38	8.13	(93.19)	
Nitrogen	0.91*	0.23	1.27	0.22	0.31	0.25	0.32	0.48	8.86	
Sulfur	-	0.13	N.A.	0.22	0.10	0.08	0.12	0.12	N.A.	
H/C	1.02*	1.38	0.83	1.48	1.39	1.32	1.28	1.28	1.14	
Analyses of Microreactor Products										
Carbon	(93.46)	86.39	90.36	87.09	88.09	87.99	88.23	88.62		
Hydrogen	9.02	10.86	7.99	11.79	11.20	10.69	10.35	9.54		
Nitrogen	0.49	0.10	0.69	0.03	0.07	0.08	0.13	0.26		
Sulfur	N.A.	<0.01	N.A.	<0.01	<0.01	<0.01	0.05	0.04		
H/C	1.16	1.51	1.06	1.62	1.53	1.46	1.41	1.29		

\* Calculated from V-178 and T-102 data.

( ) Poor reproducibility in analysis.

N.A. = Not analyzed.

Table 2. Analyses of used catalysts from microreactor runs reported as weight percent.

<u>Feed</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>
35% V-178 + 65% T-102 bottoms	11.42	1.46	0.57
V-178	1.96	0.82	0.50
T-102 bottoms	11.71	1.44	0.61
<u>V-178 Distillate Cuts</u>			
-550°F	1.25	0.82	0.55
550-650°F	1.58	0.84	0.47
650-750°F	1.92	0.90	0.46
750-850°F	2.64	0.82	0.40
+850°F	4.20	0.93	0.49

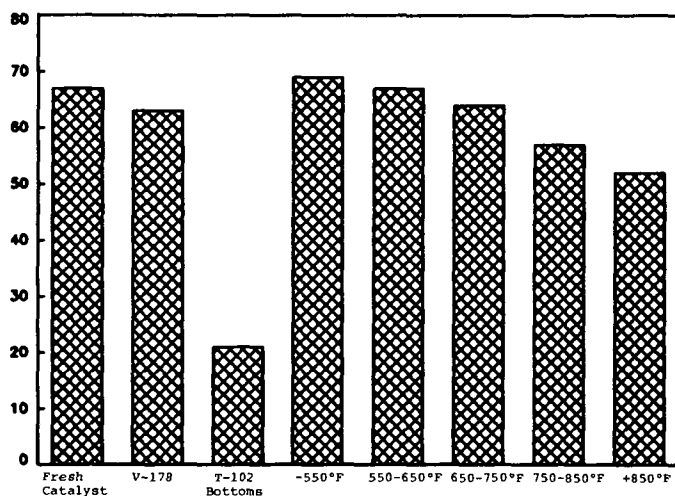


Figure 1. HDS activity of fresh catalyst and catalysts from micro-reactor runs with different feed components.

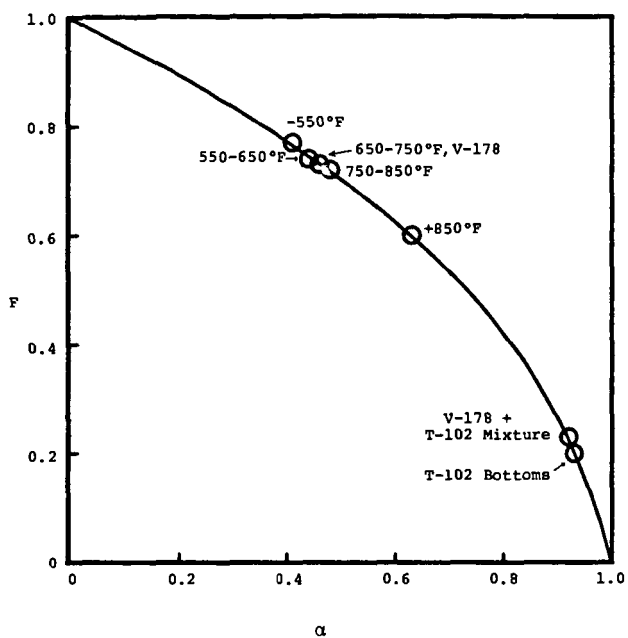


Figure 2.  $F$  vs  $\alpha$  for catalysts from microreactor experiments. Results shown for carbonaceous deposits only.